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ON THE THEORY OF THE QUENCHING OF THE FLUORESCENCE OF SOLUTIONS

by

I. M. Rozman

In an article by B. Ya. Sveshnikov [1] the methods of mathematical calculation of the quenching of the fluorescence of solutions of organic substances developed by T. Förster [2] and M. D. Galanin [3] are subjected to criticism. Without pausing to analyze this criticism, we would like to direct attention to still one other method of calculation based on Markov's well-known approach (see, for example, [4]).

Let us say that a solution contains molecules of a substance M_1 which have been directly excited by an external source of radiation and molecules of M_2 to which the energy of the electron excitation of M_1 can be transferred. In accordance with [1, 2] we will consider that return transfer is impossible, that the molecules are immobile (during the time of the excited state), and that they are distributed statistically in the solution. The probability of the transfer of energy from M_1 and M_2 depends on the optical characteristics of the molecules, their mutual distance r, and the refraction index of the medium and can be written in the form [5]:

$$w = \frac{1}{\tau_0} \frac{R_0^6}{r^6},$$

where τ_0 is the average duration of the excited state of M_1 in the absence of a transfer of energy. If in the solution there are N_2 molecules of M_2, the total probability of transfer for some excited M_1^* will be

$$W_i = \frac{1}{\tau_0} \sum_{k=1}^{N_2} \frac{R_0^6}{r_{ik}^6}.$$

Because of the presence of fluctuations in the spatial distribution of M_2 [1, 2], W_1 will have some probable distribution of F(W)dW:

$$\int_0^\infty F dW = 1.$$

Then, as can easily be seen, the law of the quenching of the fluorescence of compound 1 will be

$$N_1(t) = N_{10} e^{-\frac{t}{\tau_0}} \int_0^\infty e^{-Wt} F(W)\, dW, \tag{1}$$

and the quantum yield will be

$$\eta_1 = \eta_{10} \int_0^\infty \frac{F(W)\, dW}{1 + \tau_0 W}. \tag{2}$$

Thus the problem of determining the relation of the quantum yield and the law of quenching to the concentration of M_2 amounts to the calculation of the function of the distribution F.

The probability that W lies in the interval W ± dW or

$$-\frac{1}{2} dW + W < \frac{1}{\tau_0} \sum_{k=1}^{N_2} \frac{R_0^6}{r_k^6} < \frac{1}{2} dW + W, \tag{3}$$

is determined by the number of all possible combinations of r_k which satisfy this inequality. Let us say that the molecule which is being examined is located in the center of a sphere having a radius of R. In this the average concentration of the molecules of M_2 is

$$n_2 = \frac{N_2}{\frac{4}{3}\pi R^3} = \frac{N_2}{V}.$$

Then the probability that one from M_2 will be at a distance of r_k, $r_k + dr_k$ from M_1^* will be

$$\varphi(r_k)\, dr_k = 4\pi r_k^2 dr_k V^{-1},$$

and the probability that one of the distributions satisfying (3) will be achieved is

$$\prod_{k=1}^{N_2} \varphi(r_k)\,dr_k.$$

Consequently,

$$F(W)\,dW = \int \ldots \int \prod_{k=1}^{N_2} \varphi(r_k)\,dr_k, \tag{4}$$

where the integration proceeds only with those combinations of r_k which satisfy (3). If in accordance with Markov's method one introduces under the integral sign in (4) the Dirichlet function

$$\frac{1}{\pi} \int_{-\infty}^{\infty} dx \cdot \frac{\sin\left(\frac{dW}{2} x\right)}{x} \exp\left\{ix\left(\frac{1}{\tau_0} \sum_{1}^{N_2} \frac{R_0^6}{r_k^6} - W\right)\right\},$$

then the integration is applied to the entire interval of changes of r_k. After the transformations we obtain:

$$F(W)\,dW = \frac{1}{2\pi}\,dW \int_{-\infty}^{\infty} dx e^{-ixW} \cdot A(x),$$

where

$$A(x) = \left\{ \int_0^R \frac{4\pi r^2}{V} \exp\left(i\,\frac{xR_0^6}{\tau_0 r^6}\right) dr \right\}^{N_2}.$$

At the limit when $R \to \infty$ it is possible to use Stirling's formula and obtain

$$A(x) = \exp\left\{-4\pi n_2 \int_0^{\infty} r^2 \left[1 - \exp\left(i\,\frac{xR_0^6}{\tau_0 r^6}\right)\right] dr\right\},$$

which leads to the following formula for the normalized function of distribution[1)]

$$F(W)\,dW = \frac{1}{(2\pi)^{1/2}} \frac{g}{(W\tau_0)^{3/2}} \exp\left\{-\frac{g^2}{2W\tau_0}\right\} \tau_0 dw, \tag{5}$$

where

$$g = \frac{1}{3}(2\pi)^{3/2} R_0^3 n_2,$$

1) The author is grateful to M. Z. Maksimov for calculation of the integral.

F(W) has a maximum when

$$W\tau_0 = \frac{1}{3} g^2,$$

and with the half width

$$\Delta (W\tau_0) \approx 0.9 g^2.$$

The law of quenching and the quantum yield of fluorescence are easily calculated on the basis of formulas (1), (2), and (5)

$$N_1(t) = N_{10} \exp\left\{ -\frac{t}{\tau_0} - g\sqrt{\frac{2t}{\tau_0}} \right\}, \tag{6}$$

$$\eta_1/\eta_{10} = 1 - \sqrt{\frac{\pi}{2}}\, g e^{g^2/2} \left[1 - \Phi\left(\frac{g}{\sqrt{2}}\right)\right], \tag{7}$$

where Φ is the integral of probability.

Formulas (6) and (7) completely coincide with the corresponding formulas which were obtained in [2] and [3].

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